

Utilization Of Water-Soluble Zirconium Compounds As Drying Accelerators In Aqueous Coating Agents

The present invention relates to the use of water-soluble zirconium compounds as drying accelerators in aqueous coating compositions.

Conventional systems for quick-drying coatings are generally solventborne. In these solvent-based coating compositions, the rate of drying can be controlled by varying the solids content and/or the solvent. Aqueous coating compositions are environmentally friendly and in recent times have come more and more to replace their solvent-based counterparts. For preparing a waterborne coating composition, it is normal to use polymer dispersions as the binder.

A disadvantage of aqueous coating compositions is the dependence of the drying rate on the temperature and atmospheric humidity. At low atmospheric humidity the drying rate is generally quick, in some cases even quicker than in the case of conventional coating compositions. At high atmospheric humidities and low temperatures, however, such as in the morning and evening, for example, and before or after rainfall, the drying rate is very slow, since the evaporation of the water is greatly hindered. Such coatings then acquire rain resistance only after very long standing times. Accelerated drying of aqueous coating compositions is desirable particularly for exterior applications, such as, for example, paints for buildings, bridges, ships, and road markings, and also exterior renders.

For quick-drying aqueous coating compositions there are three different principles possessing practical relevance.

According to the flocculation principle, flocculation of the ionically stabilized binder takes place either following application of the coating composition,

which comprises a polyamine and ammonia as volatile base, as a result of the fact that the ammonia evaporates (US-A-5 527 853, EP-A-0 594 321, EP-A-0 728 822, EP-A-0 409 459) or by virtue of the fact that, together with the coating composition, an acid solution (WO 94/29 391) or a salt solution (EP-A-0 200 249, US-A-4 571 415, US-A-5 403 393) is sprayed.

A change in viscosity of the surface of the coating composition can be brought about by applying either a thickener to the fresh coating, thereby producing an increase in viscosity, as disclosed, for example, in EP-A-0 721 003, or a base to the fresh coating which comprises a thickener which, however, is not activated by formulation of a low pH.

In the case of a water absorption method, water-absorbing substances, such as silica gels, ion exchangers, polymer gels, etc., are used during the application of the coating composition.

In the case of coating compositions where drying is activated by evaporation of a volatile base such as ammonia, the scope of application is limited as a result, for example, of odor pollution. Coating compositions which are brought into contact with salts following their application have the disadvantage of being restricted to the use of weakly stabilized dispersions. The salts used must be sprayed as a solution together with the coating composition or applied subsequently by spraying or scattering. In the case of subsequent application of the salts in solid or dissolved form, considerable fractions may be washed away by rain, for example, thereby severely impairing the efficiency of the method. The quantities of salt washed away by rain generally pass into the groundwater. Consequently, this mode of drying is undesirable.

EP-A-0 709 441 discloses the use of zirconium compounds in paints and adhesives. The zirconium compounds there are used as a siccative, crosslinking reagent, thixotropic agent, free-radical scavenger in

decomposition reactions of coating films, and a complexing substance for ingredients which normally lead to bleeding and/or discoloration of surfaces.

It has surprisingly now been found that coating compositions which comprise one or more water-soluble zirconium compounds exhibit markedly accelerated drying. In particular, they do so even at low temperatures. The binders present in the coating compositions are, surprisingly, not subject to any special requirements.

For use in accordance with the invention the coating compositions contain, based on the binder, preferably up to 50% by weight, with particular preference from 0.5 to 10% by weight, and in particular from 1 to 5% by weight of zirconium compounds, calculated as zirconium oxide.

Zirconium compounds used are preferably ammonium zirconium carbonate, zirconium acetoacetate, zirconium hydroxychloride, zirconium orthosulfate, zirconium propionate and/or potassium zirconium phosphate. Particular preference is given to using ammonium zirconium carbonate.

The zirconium compounds may be added to the coating composition as solids and/or as aqueous solutions.

In addition to a binder, the zirconium-containing coating compositions may when appropriate further comprise film formers, pigments, fillers (such as titanium dioxide, talc, calcite, dolomite, for example), thickeners (such as cellulose ethers, acrylic acid, polyurethane thickeners, for example), dispersants, wetting agents, preservatives, emulsifiers and/or defoamers. The pigment volume concentration (PVC) is generally situated between 15 and 90%. In order to increase the stability of the coating composition it is possible where appropriate additionally for from 0.1 to 5% by weight, preferably from

0.5 to 1% by weight, based on the binder, of ionic and/or nonionic emulsifiers to be added to it.

The binders present in the coating compositions generally comprise polymer dispersions based on homopolymers and/or copolymers. Suitable homopolymers and copolymers include all known homopolymers and copolymers which are obtainable in dispersion form.

In one preferred embodiment the copolymers contain from 70 to 99.7% by weight, based on the overall amount of the monomers, of free-radically polymerizable olefinically unsaturated compounds from the group consisting of acrylates and methacrylates of (C₁-C₁₂) monoalcohols, preferably of (C₁-C₈) monoalcohols, examples being methanol, ethanol, isopropanol, isobutanol, n-butanol, and 2-ethylhexyl alcohol, vinylaromatic monomers, vinyl esters of (C₁-C₁₂) alkanemonocarboxylic acids, examples being vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate, [®]VeoVa 9 and [®]VeoVa 10 (Shell-Chemie, vinyl esters of α,α -dialkyl-branched monocarboxylic acids), vinyl halides, examples being vinyl chloride and vinylidene chloride, α,β -monoolefinically unsaturated nitriles, examples being acrylonitrile and methacrylonitrile, and the alkyl esters of monoolefinically unsaturated dicarboxylic acids, examples being di-n-butyl maleate and di-n-butyl fumarate.

The copolymers further contain preferably from 0.3 to 10% by weight, with particular preference from 0.5 to 5% by weight, based on the overall amount of the monomers, of α,β -monoolefinically unsaturated monocarboxylic and dicarboxylic acids, examples being acrylic acid, methacrylic acid, itaconic acid, maleic acid, and fumaric acid, and their amides with or without substitution on the nitrogen atoms, examples being acrylamide, methacrylamide, N-methylolacrylamide and N-butoxymethacrylamide.

It is also possible for from 0 to 20% by weight, preferably from 0.5 to 5% by weight, based on the overall amount of the monomers, of functional monomers to be present in the copolymers, examples being hydroxyl-containing monomers, such as hydroxyalkyl acrylates and methacrylates, especially hydroxyethyl methacrylate and hydroxypropyl methacrylate, and/or acetylacetoxy-containing monomers which improve the wet adhesion, particularly allyl acetoacetate, acetylacetoxyethyl methacrylate and acetylacetoxybutyl methacrylate, and/or monomers with a crosslinking action such as monomers containing epoxide groups and monomers containing silane groups, particular glycidyl acrylate, glycidyl methacrylate, vinyltrimethoxysilane and methacryloyloxypropyltrimethoxysilane, and/or nitrogen-containing monomers from the group consisting of polymerizable monomers containing an amino, ureido or n-heterocyclic group, examples being dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate, N-(2-methacryloylethyl)ethyleneurea, and/or monomers containing keto groups, examples being diacetone acrylamide, diacetone methacrylamide, acrolein, and 2-butanone methacrylate.

In self-crosslinking dispersions, polymers containing keto groups may also contain up to 5% by weight, based on the overall amount of the monomers, of a difunctional or polyfunctional carboxylic hydrazide, an example being adipic hydrazide.

The binders may where appropriate further comprise emulsifiers, protective colloids, additives, auxiliaries and/or noncopolymerizable crosslinkers.

Examples of suitable nonionic emulsifiers include alkyl polyglycol ethers and ethoxylation products of polypropylene oxide. Suitable ionogenic emulsifiers include primarily anionic emulsifiers, such as alkali metal salts or ammonium

Suitable protective colloids include natural substances, such as gum arabic, starch, and alginates, for example, or modified natural substances, such as cellulose derivatives, for example, or synthetic polymers, such as polyvinyl alcohol and polyvinylpyrrolidone, for example, or mixtures thereof.

In the widest sense, the coating compositions of the present invention may also comprise adhesives, pastes, putties, sealing compounds or pressure compensation coatings for exterior insulation and finish systems.

The invention is described in more detail below with reference to examples, without being restricted thereby.

A) Preparation of synthetic-resin renders

The synthetic-resin renders described in the inventive and comparative examples have the base formula indicated in Table 1.

Preparation of a comparative render 1 containing no zirconium compound

The composition of the comparative render 1 corresponds to the base formula indicated in Table 1 in which the binder used comprises a synthetic-resin dispersion Mowilith® DM 2452 (Table 1, ingredient 8) from Clariant GmbH having a solids content of 50%, a pH of 6, and a viscosity of 400 mPas. The monomer basis of this dispersion is formed by vinyl acetate, vinyl esters of Versatic acid®, and acrylates.

To prepare the render, the water is introduced initially and the remaining ingredients are added in the order stated, with mixing. After the raw materials have been introduced, the render is mixed until completely homogeneous.

Table 1: Base formula of a synthetic-resin render

Ingredients	Parts by weight
1. Water	56.9
2. Cellulose ether (type MC, medium viscosity)	1.5
3. Dispersant (polyacrylate)	3.0
4. Preservative (isothiazolinone)	2.0
5. Wetting agent (polyphosphate)	0.6
6. Sodium hydroxide solution, 10%	2.0
7. Defoamer (based on mineral oil)	2.0
8. Synthetic-resin dispersion	140.0
9. Pigment (titanium dioxide)	20.0
10. Filler (kaolin 3 μm)	20.0
11. Filler (calcite particle size 40 μm)	150.0
12. Filler (calcite particle size 130 μm)	170.0
13. Filler (calcite 130 μm – 500 μm)	100.0
14. Texturing grain (calcite 1.5 – 2.0 mm)	300.0

15. Auxiliary film former (aliphatic hydrocarbon)	4.0
16. Auxiliary film former (glycol ether)	6.0
17. Fiber (polyethylene)	2.0
	980.0

Example 1:

Preparation of a zirconium-containing synthetic-resin render 1.

The composition of synthetic-resin render 1 differs from the base formula indicated in Table 1 only in that it further contains 20 parts by weight of a zirconium compound Bozefix PAS5200 from Clariant GmbH. The binder used is the same synthetic-resin dispersion as in comparative example 1.

To prepare the render, the water is introduced and the remaining ingredients are added in the order stated, with mixing, the zirconium compound being added last. After the raw materials have been introduced, the render is mixed until completely homogeneous.

Comparative example 2:

Preparation of a comparative render 2 containing no zirconium compound.

The composition of comparative render 2 corresponds to the base formula indicated in Table 1 with the binder used being a synthetic-resin dispersion Mowilith® LDM 1880 (Table 1, ingredient 8) from Clariant GmbH having a solids content of 55%, a pH of 5 and a viscosity of 2000 mPas. The monomer basis of this dispersion is formed by vinyl acetate and ethylene. Comparative render 2 is prepared in the same way as comparative render 1 as described in comparative example 1.

Example 2:

Preparation of a zirconium-containing synthetic-resin render 2.

The composition of synthetic-resin render 2 differs from the base formula indicated in Table 1 only in that it further contains 20 parts by weight of a zirconium compound Bozefix PAS5200 from Clariant GmbH. The binder used is the same synthetic-resin dispersion as in comparative example 2.

To prepare the render, the water is introduced and the remaining ingredients are added in the order stated, with mixing, the zirconium compound being added last. After the raw materials have been introduced, the render is mixed until completely homogeneous.

B) Performance testing of comparative renders 1 and 2 and of the zirconium-containing synthetic-resin renders 1 and 2.

a) Preparation of test specimens

The substrate, comparative renders 1 and 2, synthetic-resin renders 1 and 2, and the mold required are conditioned in a climate chamber to the test temperature of 5°C. At this temperature, the renders are applied to a fiber cement panel with the dimensions 10 cm x 15 cm, using a trowel, and are then drawn off to the thickness of the grain, and textured.

b) Testing of the test specimens

After different drying times at a test temperature of 5°C, the test specimens are examined for their degree of drying. To this end the test specimens are each sprayed with 60 grams of water. The water mist is generated using a commercial atomizer. During the spraying operation, the test specimens are situated upright. The liquid running off is collected quantitatively. While the coating composition has not yet dried, the test liquid washes particles out, and as a result acquires a whitish discoloration. The intensity of discoloration allows conclusions to be drawn about the drying state of the coating composition.

The degree of drying of the renders is assessed in accordance with the 6 classes listed in Table 2.

Table 2: Classification of the degrees of drying

Class	Degree of drying	Coloration of the test liquid
1	Dry	No coloration
2	Almost dry	Slight clouding
3	Partly dry	Clouding
4	Damp	Severe clouding
5	Wet	White
6	Very wet	Very white

The degrees of drying of comparative renders 1 and 2 and of synthetic-renders 1 and 2 in accordance with the 6 classes of Table 2 after 4 and 7 hours' drying time at a drying temperature of 5°C are indicated in Table 3.

Table 3: Degrees of drying of the renders investigated

Coating composition	Degree of drying after 4 hours' drying time	Degree of drying after 7 hours' drying time
Comparative render 1	4	2 to 3
Synthetic-resin render 1	2	1 to 2
Comparative render 2	3	2
Synthetic-resin render 2	2	1

As is evident from Table 3, the zirconium-containing synthetic-resin renders 1 and 2 exhibit in every case a higher degree of drying than the comparative renders 1 and 2, irrespective of the binder (synthetic-resin renders 1 and 2 contain different synthetic-resin dispersion binders) and irrespective of the drying time.